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Annual export production in the interior Weddell Gyre estimated from a chemical mass balance of nutrients

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Abstract

Nitrate, phosphate and silicate data are presented from 1992 austral winter and 1998 austral autumn cruises with “FS *Polarstern*” in the Weddell Gyre. Because in the Weddell Gyre, away from the boundary current, the surface layer is eventually formed from upwelled deep water, the difference in nutrient concentrations between these layers can be used to compute net nutrient consumptions (identical with the export production). This method renders a value for the export production that is based on observed annual changes. The results are consistent for two years and two regions within the central gyre. The calculated net nitrate and phosphate consumptions were scaled to net carbon consumptions using canonical Redfield ratios, yielding $16\text{--}17\ \mu\text{mol C kg}^{-1}\text{ yr}^{-1}$. This equals $21 \pm 4\ \text{g C m}^{-2}\text{ yr}^{-1}$ as a robust estimate for the marginal ice zone. The net annual silicate consumption in the surface layer, which equals the export of biogenic silica, amounts to $15\text{--}18\ \mu\text{mol kg}^{-1}\text{ yr}^{-1}$. There is a tendency for higher values in the eastern Weddell Gyre. The estimated silicate consumption of about $1.8\ \text{mol Si m}^{-2}\text{ yr}^{-1}$ is relatively high compared to earlier estimations of biogenic silica export. The silicate to carbon consumption ratio of about 1 is very high, and documents the dominance of diatoms in the export of organic material. © 2002 Elsevier Science Ltd. All rights reserved.

Résumé

Sont présentées les distributions verticales de nitrate, de phosphate et de silicate en Mer de Weddell, pour les périodes de l'hiver austral 1992 et de l'automne austral 1998. Les eaux de surface du tourbillon à grande échelle de la Mer de Weddell (temps de résidence égal à 2.9 ans) sont formées par l'upwelling des eaux profondes. La différence de concentrations des sels nutritifs entre les couches profondes et de surface permettent de calculer la consommation annuelle, équivalente à la production exportée de l'élément nutritif considéré vers les couches profondes. Les résultats sont comparables pour les deux scénarios annuels étudiés. La production exportée de carbone pour les eaux de surface de la zone marginale de la glace, calculée à partir des consommations annuelles en nitrates et phosphates après transformation grâce aux rapports de Redfield, est estimée à $16\text{--}17\ \mu\text{mol C kg}^{-1}\text{ yr}^{-1}$ soit en moyenne $21 \pm 4\ \text{g C m}^{-2}\text{ yr}^{-1}$. La consommation annuelle de silicate est estimée à $1.8\ \text{mol Si m}^{-2}\text{ yr}^{-1}$, relativement élevée en

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comparaison des estimations antérieures. Le rapport molaire Si/C, voisin de 1 dans le matériel exporté, traduit la dominance des diatomées dans l'export de matières organiques.

1. Introduction

Photosynthesis in the oceanic surface layer triggers the uptake of atmospheric carbon dioxide, thus contributing to the regulation of the atmospheric CO₂ content. In climate history, this process has been an important forcing factor for the extent of greenhouse potential exerted by atmospheric CO₂. For the oceans, the term biological pump is used: organic matter, whether particulate or dissolved, is produced in the surface layer and transported to deeper water layers where it is degraded and CO₂ and nutrients are released, as if pumping down CO₂ and nutrients against their vertical gradient. On a global scale in the oceans, the biological pump is counteracted by the upwelling of CO₂ and nutrient-rich deep water. Present or future global change may have impact on the capacity of the biological pump, where both positive and negative feedbacks are conceivable.

In the Southern Ocean, upwelling of deep water occurs, which reaches the surface layer in the Antarctic Divergence. These deep waters partly derive from other oceans, where due to surface production and deep respiration the deep water already has become oversaturated with CO₂ and undersaturated with O₂. Within the Southern Ocean, the competition between upwelling of these CO₂ oversaturated waters and the local biological pump determines whether this region is a net source or a net sink of atmospheric CO₂. Recently, the indications for a sink have become compelling, both based on CO₂ measurements and modelling (e.g., Metzl et al., 1999; Louanchi et al., 1999; Lancelot et al., 2000). However, from a biological point of view, the extent of the biological pump is not well known. The so-called export production has been determined by means of shallow sediment traps, which collect material sinking from the surface layer. Trapped material in the Southern Ocean exhibits orders of magnitude spatial and temporal variations (Fischer et al., 1988; Karl et al., 1991), which seriously hampers extrapolation from the few points in space and time to an

annual export estimate over larger areas. The efficiency of sediment traps at any depth is also a subject of concern (Buesseler, 1991). Finally, sediment traps do not include the possible export of dissolved material, and thus they intrinsically underestimate the export production. Using ²³⁴Th deficiencies, an estimate of export production also can be obtained (Rutgers van der Loeff et al., 1997). Like other methods (see below), the ²³⁴Th deficiencies method provides local, in situ estimations for the export production, which must be interpolated or extrapolated to obtain annual estimates.

Another concept for estimating the effect of the biological pump relies on the fact that over longer time scales, the new production equals the export production (Williams, 1993). New production is that part of the primary production that is fuelled by new nitrate, as opposed to nitrogen from regenerated sources in the surface layer, like ammonium and urea. The nitrate uptake is determined from incubations of samples collected in different seasons. For obtaining an annual estimate of new production, assumptions as to the duration and intensity of the uptake have to be made, which restricts the use of this method. This disadvantage can be overcome by determining seasonal nutrient depletions or recording the subsurface oxygen maximum (Jennings et al., 1984; Jenkins and Goldman, 1985). These methods inherently integrate over larger space and time scales. Recently, we used such a method to study the opposing effects of upwelling and biological drawdown on the CO₂ concentration in the Weddell Sea surface layer (Hoppema et al., 1999) and found that the latter effect prevails over the former one.

In this study, we exploit the particular hydrographic conditions in the Weddell Gyre for estimating the net nutrient consumption in the surface layer by means of a chemical mass balance to derive truly annual export productions. We use data collected during a recent cruise in different parts of the gyre and compare this with previous data

from the same areas. This will allow us to examine the consistency of the method and to assess the effect of interannual and spatial variability.

2. Methods and data

During cruise ANT XV/4 in April–May 1998 with the German research vessel “FS *Polarstern*”, a hydrographic survey was done of the Weddell Gyre including the Weddell–Scotia region (Fahrbach, 1999). We show data of two transects across the Weddell Gyre, one on the prime meridian and one in the western Weddell Sea (Fig. 1). A suite of parameters was measured, of which we present the major nutrients nitrate, phosphate, silicate and nitrite. In addition, we use nutrient data of “*Polarstern*” cruise ANT X/4 of June–July 1992 (Lemke, 1994) from the identical transect along the prime meridian and from the western Weddell Sea. Part of the ANT X/4 data have appeared in Hoppema et al. (1998). Potential temperature and salinity were obtained with a CTD instrument, accuracy 0.003°C and 0.003 (practical salinity scale), respectively.

During cruise ANT XV/4 (1998), nutrient concentrations were analysed using standard

photometric methods on a Technicon TRAACS 800 rapid flow autoanalyser. Accuracy was set with stock standards daily diluted in low nutrient seawater. These primary stocks had been prepared in the home laboratory by weighing. A reference standard, containing a mixture of nitrate, phosphate and silicate, also was measured at every run and used for statistical purposes and data correction. The precision, obtained from 21 duplicates, when all rosette bottles were fired at one depth, was $0.07\text{ }\mu\text{mol kg}^{-1}$ (0.19%) for nitrate + nitrite, $0.004\text{ }\mu\text{mol kg}^{-1}$ (0.18%) for phosphate and $0.3\text{ }\mu\text{mol kg}^{-1}$ (0.23%) for silicate. For further details, refer to Bakker (1999). Nutrient data of cruise ANT X/4 (1992) were obtained with a Technicon Autoanalyser-II system. All samples were analysed in duplicate. The estimated precision was $0.1\text{ }\mu\text{mol kg}^{-1}$ for nitrate, $0.01\text{ }\mu\text{mol kg}^{-1}$ for phosphate and $0.3\text{ }\mu\text{mol kg}^{-1}$ for silicate.

3. Computational aspects

Our method for determining the net biological utilisation of nutrients is based on the specific hydrographic conditions in the Weddell Gyre. The

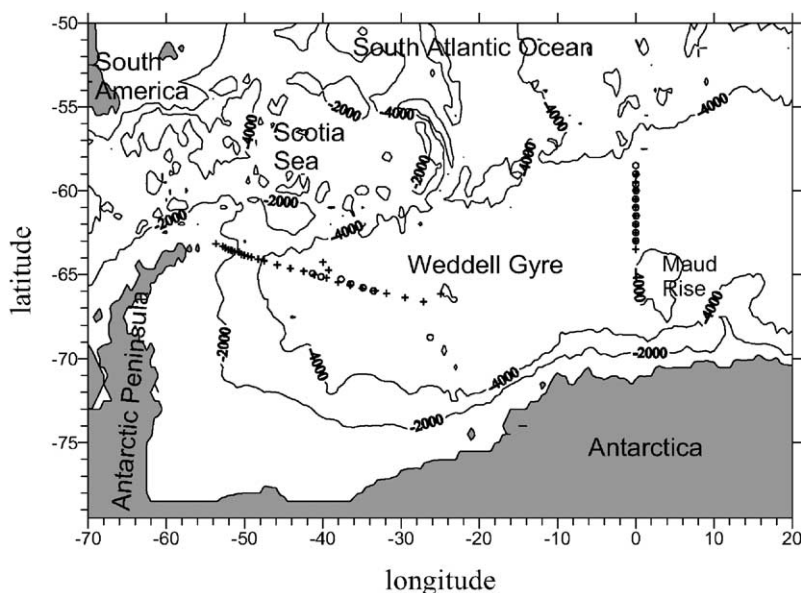


Fig. 1. Map of the Weddell Gyre and neighbouring areas with location of stations. Circles denote stations of cruise ANT X/4 (1992) and crosses those of cruise ANT XV/4 (1998).

deep water of the gyre is fed with Lower Circumpolar Deep Water (LCDW) from the Antarctic Circumpolar Current (Whitworth and Nowlin, 1987). This LCDW, locally called Warm Deep Water (WDW) because it features a temperature maximum, occurs directly underneath the surface layer. As the Weddell Gyre is a divergent feature, upwelling of WDW occurs towards its interior. The deep water is transported into the surface mixed layer by entrainment during the autumn and winter period (Gordon and Huber, 1990), also evident from water-mass transformation calculations (Fahrbach et al., 1994). As the surface waters from the margins and from the central gyre are spatially well separated (Rutgers van der Loeff, 1994), this implies that the surface water of the central Weddell Gyre derives exclusively from the underlying WDW. This is illustrated schematically in Fig. 2. If one water mass derives from the other, it should hold: $[SW(X)] = [WDW(X)]$, where $[SW(X)]$ and $[WDW(X)]$ are concentrations of any property in the surface layer and the WDW, respectively. Obviously, this is not what is observed because

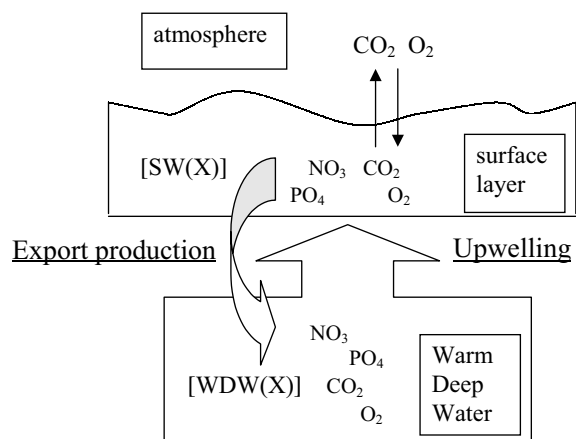


Fig. 2. Schematic representation of a cross section of the central Weddell Gyre upper water column and atmosphere. Properties are transported from the WDW into the surface water by physically mediated upwelling. Biologically mediated is the downward transport of nitrate (NO_3), phosphate (PO_4), carbon dioxide (CO_2) and oxygen (O_2). CO_2 and O_2 are also exchanged with the atmosphere. $[SW(X)]$ and $[WDW(X)]$ are the concentrations of any property in the surface water and WDW, respectively.

many processes occur in the surface layer that modify the concentrations. For example, air–sea exchange causes changes for CO_2 and oxygen (Fig. 2). Nitrate and phosphate are lower in the surface water than in the WDW (Fig. 3), which is exclusively caused by utilisation of nutrients for producing organic material. Hence, in this case $[WDW(\text{NO}_3)] - [SW(\text{NO}_3)] = \Delta(\text{NO}_3)_{\text{bio}}$ and $[WDW(\text{PO}_4)] - [SW(\text{PO}_4)] = \Delta(\text{PO}_4)_{\text{bio}}$, where $\Delta(\text{NO}_3)_{\text{bio}}$ and $\Delta(\text{PO}_4)_{\text{bio}}$ are the changes due to biological activity in nitrate and phosphate, respectively. Thus, the difference of the nutrient concentrations between the WDW and the surface water is a measure for the nutrient consumption.

The chemical mass balance approach has been applied previously (e.g., Jennings et al., 1984; Ishii et al., 1998; Rubin et al., 1998; Hoppema et al., 2000). In these studies, the net nutrient consumption was obtained from the difference between the surface layer and the Winter Water remnant layer below it, the latter of which occurs in spring and summer as a temperature minimum. Such methods yield the net consumption until the moment of sampling, mostly in summer or early autumn. Our method determines the difference between the surface layer in winter and the subsurface layer beneath the permanent pycnocline from which the surface layer originates. Provided we know the residence time of the surface layer, which is usually more than 1 yr, we will obtain the true net nutrient consumption on an annual basis.

The residence time of the surface layer with respect to WDW entrainment has been calculated by Hoppema et al. (1999) using the decrease of the oxygen concentration in the surface layer from April (ice covered) to December (temperature minimum layer), which was attributed to the oxygen-poor WDW. Thus the entire period of entrainment was captured. Hoppema et al. (1999) estimated the residence time to be 2.9 ± 0.5 yr for the western Weddell Sea interior. This residence time is for a different year as the data in the present study, and thus interannual variability may influence the results. For the prime meridian area, Gordon and Huber (1990) report a mean residence time of 2.5 yr, which is within the error of the above estimate. It thus appears that interannual variability is probably relatively small.

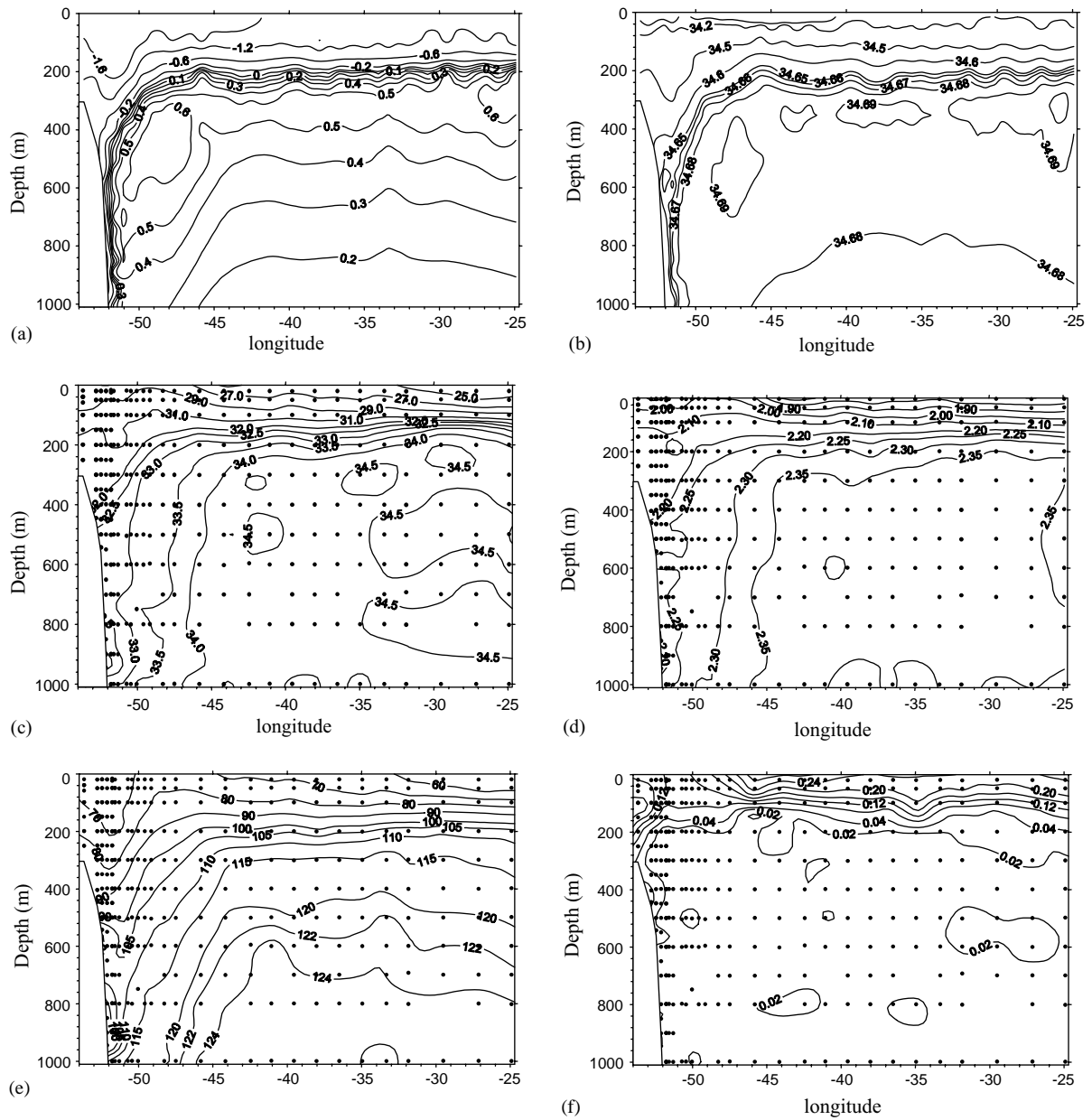


Fig. 3. Vertical sections of the upper 1000 m contoured for potential temperature (a), salinity (b), nitrate (c), phosphate (d), silicate (e) and nitrite (f) between Joinville Island, at the tip of the Antarctic Peninsula (left) and the central Weddell Sea (25°W). Data are from cruise ANT XV/4, April 1998. All concentrations are in $\mu\text{mol kg}^{-1}$, potential temperature in $^{\circ}\text{C}$.

Therefore, we take 2.9 yr as the mean age of the surface layer.

The timing for the determination of the difference between the surface layer and the WDW layer

is important, because the surface layer nutrient concentrations vary seasonally. In summer, the nutrient concentrations in the surface layer are the lowest due to active photosynthesis. In late

summer and autumn, the concentrations increase again because of remineralisation, and winter nutrient concentrations are the highest (Clarke and Leakey, 1996; Gibson and Trull, 1999). Thus, using summer nutrient data would result in a relatively large WDW–surface water difference. Using winter nutrient data results in a smaller difference, but then this is not affected by active production and thus is exclusively caused by net nutrient consumption, i.e. it represents the so-called export production.

There are some implicit assumptions in our method: (1) interannual variability, both in the surface and WDW layers, is negligible; (2) advection of surface and subsurface waters is small; and (3) active biological production and/or remineralisation in winter is negligible. As to point (1), we use data from different years (1992 and 1998), which should enable an assessment of interannual variability. As to (2), horizontal current velocities in the inner gyre are extremely low (Fahrbach et al., 1994), which minimises the effects of advection. Current velocities in the Weddell Sea margins are much larger. Therefore, we omit the coastal current region from our analysis and use only data of the interior of the gyre. As to (3), literature data indicate that some biological activity occurs in winter, but the extent is small compared to the other seasons. We touch upon this at several occasions further on.

We calculate the depth-integrated mean concentrations of nitrate, phosphate and silicate in surface water. When a completely homogeneous surface layer was found (e.g., during winter cruise ANT X/4 in June/July) the depth-integrated mean value per station was simply the mean of all surface layer data points. In cases when the winter surface layer was not yet fully developed (cruise ANT XV/4, April/May), the elevated lower-surface-layer concentrations were accounted for proportionally to their depth range. The lower bound of the surface layer was determined from downcast CTD temperature data; this is either the temperature minimum depth or the maximum depth of the temperature minimum (when the temperature minimum occurred at the sea surface). In the latter case, the criterion for the temperature difference is 0.3°C. At the same stations, the

concentrations of nitrate, phosphate and silicate of the WDW were established at the depth of the temperature maximum at about 250–300 m (Fig. 3a), which generally occurs directly below the pycnocline. At or close to this depth, nutrient maxima were observed. This excludes silicate (Fig. 3e), which exhibits a continuous increase with depth, with the silicate maximum occurring at about 1000–1500 m (Whitworth and Nowlin, 1987; Hoppema et al., 1998). However, at or just below the temperature maximum the vertical gradient in the silicate concentration sharply changes.

Using the nutrient difference between the WDW and surface layers we compute the net carbon consumption, which equals the export production (see below), as follows:

$$\begin{aligned} \text{Export production (mol C m}^{-2} \text{ yr}^{-1}) \\ = [\Delta(\text{PO}_4)_{\text{bio}} (\mu\text{mol kg}^{-1}) \times 10^{-3} / \tau_{\text{sl}} (\text{yr})] \\ \times r_{\text{C:P}} \times \rho (\text{kg dm}^{-3}) \times z_{\text{WML}} (\text{m}), \end{aligned}$$

where τ_{sl} is the residence time of the surface layer with respect to upwelling (see above), $r_{\text{C:P}}$ is the Redfield ratio of C to P, ρ is the density of the surface water and z_{WML} is the winter mixed layer depth. $\Delta(\text{PO}_4)_{\text{bio}}$ is obtained from the difference between WDW and surface layer. Analogously, such a calculation is done for $\Delta(\text{NO}_3)_{\text{bio}}$. Details of the calculations are presented in Section 5.1.

4. Results

Nitrate, phosphate, silicate and nitrite sections are portrayed for the western Weddell Sea, off the tip of the Antarctic Peninsula into the central basin. The mixed-layer depth is about 100 m in the centre, but much deeper in the coastal region (Fig. 3a). In the pycnocline below the mixed layer, the nutrient gradients are large. The subsurface water in Fig. 3 belongs to the WDW layer, characterised by a temperature and salinity maximum. Except for nitrite, the concentrations are low in the surface layer and high in the WDW beneath, where nutrient maxima are found. It is worth adding that as surface concentrations they represent very high values. Towards the coast (west of 45°W), the water column structure is

rather different due to the different hydrographical regime. The structures of the distributions of nitrate and phosphate are rather similar, in contrast to that of silicate, which increases monotonically through the intermediate water. This points to different biogeochemical dynamics of silicate. The vertical distribution of nitrite is opposite to that of the other nutrients, with nearly zero concentration in the subsurface waters and a maximum at the sea surface. Near the surface, nitrate, phosphate and silicate decrease from the coast to the central basin. In the intermediate layer, there is a trend towards higher concentrations in the central basin. The lateral nitrite maximum is observed just outside the coastal current area (near 45°W). The other nutrients exhibit a local maximum near this position. Offshore of the coastal region, the lateral variation is relatively small. Very similar vertical distributions of these nutrients are observed at the prime meridian.

The mean differences between the surface water and WDW concentrations along four transects through the Weddell Gyre are gathered in Table 1 (for positions see Fig. 1). The calculated nitrate differences are variable for the different months, although most results still overlap. The largest nitrate difference (for the western Weddell Sea, mid-winter) coincides with the largest phosphate difference, but the latter is not a similarly outstanding value. This large nitrate difference is due

both to relatively low mean surface concentrations and to relatively high concentrations in the WDW (Table 1). The phosphate differences for the four transects are consistent with each other, with a slight trend towards higher values in the west as compared to the prime meridian. This trend is due to somewhat higher phosphate concentrations in the WDW in the former area (Table 1). In contrast, the silicate difference in the western Weddell Sea tends to be lower than at the prime meridian, which is caused by higher surface layer concentrations in the former region. Apart from nitrate, the differences for phosphate and silicate are not at variance for the two years of measurements. This strongly suggests that interannual variability is small.

From the WDW–surface water differences (Table 1), annual net nutrient consumptions were computed using the residence time of the surface layer of 2.9 ± 0.5 yr (see Section 3). Using the classical Redfield ratios, the phosphate and nitrate consumptions were scaled to carbon consumptions. Results appear in Table 2 and are discussed below.

5. Discussion

Surface layer concentrations of nitrate and phosphate as observed during cruise ANT XV/4 (Fig. 3) in April 1998 are somewhat lower than

Table 1

Mean concentrations (\pm standard deviation) of nitrate, phosphate and silicate in the surface and WDW layers and their differences for the central Weddell Gyre

	ANT XV/4, west Weddell Sea ($n = 15$) April 1998	ANT X/4, west Weddell Sea ($n = 8$) July 1992	ANT XV/4 prime meridian ($n = 11$) May 1998	ANT X/4 prime meridian ($n = 10$) June 1992
Nitrate surface	27.65 ± 0.91	25.91 ± 1.44	27.07 ± 0.53	25.78 ± 0.71
Nitrate WDW	34.64 ± 0.33	35.39 ± 0.53	34.36 ± 0.31	33.90 ± 0.63
Phosphate surface	1.901 ± 0.045	1.916 ± 0.053	1.906 ± 0.027	1.898 ± 0.053
Phosphate WDW	2.376 ± 0.016	2.409 ± 0.034	2.356 ± 0.023	2.349 ± 0.053
Silicate surface	70.3 ± 5.9	73.6 ± 4.2	57.0 ± 5.0	65.4 ± 5.2
Silicate WDW	115.6 ± 2.0	117.9 ± 2.2	111.7 ± 3.6	115.6 ± 2.9
Nitrate difference	6.99 ± 0.97	9.48 ± 1.53	7.29 ± 0.61	8.12 ± 0.95
Phosphate difference	0.475 ± 0.048	0.493 ± 0.063	0.450 ± 0.035	0.451 ± 0.075
Silicate difference	45.3 ± 6.2	44.3 ± 4.7	54.7 ± 6.2	50.2 ± 6.0

Cruise, month and year of measurements are indicated. All concentrations in $\mu\text{mol kg}^{-1}$ and normalised to salinity 35.

Table 2

Net annual consumptions of phosphate, nitrate and silicate (the latter separated between western and eastern Weddell Gyre) and calculation of the net annual carbon consumption from the nitrate and phosphate consumptions using different Redfield ratios; the Redfield et al. (1963) scaling is considered to yield the optimal results

Carbon:phosphorus	Calculated net annual carbon consumption ($\mu\text{mol kg}^{-1} \text{yr}^{-1}$)
106 (Redfield et al., 1963)	17.4 ± 3.7
117 (Anderson and Sarmiento, 1994)	19.2 ± 4.1
90 (Rubin et al., 1998; Hoppema et al., 2000)	14.8 ± 3.2
Mean phosphate difference: $0.467 \pm 0.057 \mu\text{mol kg}^{-1}$	
Net annual phosph. consumption: $0.161 \pm 0.035 \mu\text{mol kg}^{-1} \text{yr}^{-1}$	
Carbon:nitrogen	Calculated net annual carbon consumption ($\mu\text{mol kg}^{-1} \text{yr}^{-1}$)
6.6 (Redfield et al., 1963)	16.2 ± 3.4
7.3 (Anderson and Sarmiento, 1994)	18.0 ± 3.8
Mean nitrate difference: $7.14 \pm 0.81 \mu\text{mol kg}^{-1}$	
Net annual nitrate consumption: $2.46 \pm 0.52 \mu\text{mol kg}^{-1} \text{yr}^{-1}$	
Mean silicate difference, west: $44.8 \pm 5.5 \mu\text{mol kg}^{-1} \text{yr}^{-1}$	
Net annual silicate consumption, west: $15.4 \pm 3.4 \mu\text{mol kg}^{-1} \text{yr}^{-1}$	
Mean silicate difference, east: $52.5 \pm 6.1 \mu\text{mol kg}^{-1} \text{yr}^{-1}$	
Net annual silicate consumption, east: $18.1 \pm 3.9 \mu\text{mol kg}^{-1} \text{yr}^{-1}$	

winter values from the Weddell Gyre found in the literature (Nöthig et al., 1991; Cota et al., 1992; Scharek et al., 1994). Because our phosphate and nitrate data from mid-winter are comparable to or lower than our April data (Table 1), this indicates that those literature data are relatively high. All distributions reveal spatial variations, which may thus explain part of the discrepancy. Another explanation may be standardisation differences, which is not unusual for data from different laboratories. However, the magnitude of the nitrate maximum of the west Weddell Sea (Nöthig et al., 1991) and the phosphate and nitrate maxima near the prime meridian (Scharek et al., 1994) appear to be comparable to those in our data, which suggests that standardisation differences are not large.

Nitrite is an intermediate product in the nitrification process (the formation of nitrate from ammonium). The occurrence of nitrite is indicative of active or recent heterotrophic activity (degradation of organic material), since nitrite is thermodynamically unstable. In the WDW, nitrite is very low, suggesting that active heterotrophic activity there is very low or absent. Upwelling of WDW

tends to decrease the nitrite concentration in the surface layer. The fact that the winter concentration of nitrite in the surface layer is not negligible against a falling trend implies that heterotrophic activity continues in the winter. However, the nitrite concentration is only $0.2\text{--}0.3 \mu\text{mol kg}^{-1}$, so that its effect on the nitrate concentration is small. Because nitrite is short-lived in the surface layer, it is not possible to deduce the nitrite production from the difference between the WDW and surface layer, like we do for the other nutrients.

The WDW–surface water difference for nitrate in the west Weddell Gyre in July is anomalously large, and also the value in June at the prime meridian is higher than earlier in the year (Table 1). Only slight corresponding variations for phosphate were found. Apparently, between autumn and winter, nitrate and phosphate got seriously decoupled. There are two possible explanations. First, variable Redfield ratios for uptake due to variations in the phytoplankton population. For the Ross Sea, large differences between N:P uptake for diatoms and non-diatoms (mostly *Phaeocystis*) have been observed (Arrigo et al., 1999). Although diatoms dominate in the

Weddell Sea, at times also other phytoplankton may be important for nutrient uptake and export. Second, high nitrate uptake rates in winter, as reported by Cota et al. (1992) for the wintertime Weddell–Scotia region. These authors observed low carbon fixation rates, but nitrogen uptake rates similar to rates in other seasons. According to them, this is caused by a highly significant heterotrophic uptake of nitrogen, probably by bacteria. Also Whitehouse et al. (1996) noted anomalous apparent nitrate uptake as compared to phosphate and silicate uptake. Previously, Smith and Harrison (1991) discussed the uncoupling between the carbon and nitrogen cycles in the Weddell Sea. Therefore, it is not advisable to use winter nitrate deficits for scaling to carbon export production. Phosphate appears to be more appropriate; indeed Gibson and Trull (1999) observed that towards autumn the phosphate concentration increased faster than that of nitrate and silicate.

5.1. Annual net nutrient and carbon consumptions

The average net annual phosphate consumption was calculated from all four cruises/areas (Table 2). For nitrate, the analogous rate is obtained from the mean of only the April and May data (see previous section). The nitrate to phosphate consumption ratio equals 15.0, which is the global average as based on a worldwide dataset (Fanning, 1992) and close to the canonical Redfield et al. (1963) value of 16. Choosing the appropriate Redfield ratios for conversion to carbon consumptions is not trivial, because several studies have reported deviations, also in Antarctic waters (Karl et al., 1991; de Baar et al., 1997; Rubin et al., 1998; Bates et al., 1998; Arrigo et al., 1999). Anderson and Sarmiento (1994) determined remineralisation ratios in a comprehensive study covering all oceans basins, except the Southern Ocean. As the ratios were found to be approximately constant for all ocean basins and depths, we presume this also holds for southern waters. Although their ratios are on average somewhat higher than the canonical Redfield ratios, they are not significantly different. Also, from other investigations there are many indications that, despite some variability,

the Southern Ocean can be considered to be Redfieldian with respect to P, N and C (Bates et al., 1998; Gibson and Trull, 1999; Hoppema and Goeyens, 1999). Therefore, we consider the net carbon consumptions as scaled with the Redfield et al. (1963) ratios to be the optimal values. To give an idea about the uncertainty caused by using other ratios, we display those additional conversions in Table 2 as well.

Net carbon consumptions derived from nitrate and phosphate amount to 16.2 and $17.4 \mu\text{mol kg}^{-1} \text{yr}^{-1}$, respectively, which is identical within the error ranges (Table 2). This is somewhat lower than a previous estimate for the western Weddell Sea of $19 \mu\text{mol kg}^{-1} \text{yr}^{-1}$ (Hoppema et al., 1999), but again within the error intervals. Taking a mean winter mixed-layer depth of 100 m , the present value is converted to $21 \pm 4 \text{ g C m}^{-2} \text{yr}^{-1}$ (see Section 3 for formula). Before comparing this with literature data, again we point to the fact that our net carbon consumption is identical with the so-called export production. On an annual basis, this is equal to the new production (Williams, 1993). Smith and Nelson (1990) estimated the new production in the western Weddell Sea to be as high as $49 \text{ g C m}^{-2} \text{yr}^{-1}$. On the other hand, Wefer and Fischer (1991) estimate only $4 \text{ g C m}^{-2} \text{yr}^{-1}$, based on a sediment trap at 360 m depth. Apart from inherent uncertainties with the latter technique, it should be realised that this estimate only incorporates the particulate carbon export. Smith (1991) estimated the mean new production of the Southern Ocean to be $2.4 \text{ g C m}^{-2} \text{yr}^{-1}$ for the open ocean and $23 \text{ g C m}^{-2} \text{yr}^{-1}$ for ice-edge systems, based on incubation measurements. Jacques (1991) and Chavez and Toggweiler (1995) come to crude new-production estimations of 27 and $14 \text{ g C m}^{-2} \text{yr}^{-1}$, respectively, based on large-scale arguments of a physical nature. The latter value is probably too low because of the assumed too large areal extent of the calculation. Thus, our estimate fits well into this range, and only the sediment-trap based value appears too low. The central Weddell Gyre should be considered a typical ice-edge system.

The net annual silicate consumption, identical to the biogenic silica export to deeper layers, appears

to be somewhat higher at the prime meridian than in the west Weddell Sea (Table 2). Qualitatively, this agrees with adjoint model calculations on silica export for the Weddell Gyre (Usbeck, 1999). It is also in line with the surface water distribution of silicate, which shows substantially lower silicate concentrations in the eastern than in the western Weddell Gyre (Van Bennekom et al., 1988). For the Maud Rise area, just south of our area of investigation at the prime meridian, the latter authors crudely estimate the biogenic silica export to be $100 \text{ g SiO}_2 \text{ m}^{-2} \text{ yr}^{-1}$, which equals $1.7 \text{ mol Si m}^{-2} \text{ yr}^{-1}$. This figure compares well with our estimate for the prime meridian, which is about $1.8 \text{ mol Si m}^{-2} \text{ yr}^{-1}$ (converted using a surface layer depth of 100 m). However, for the offshore Weddell region, Van Bennekom et al. (1988) presented a substantially lower estimate for exported silica. For the western Weddell Sea along our transect, Leynaert et al. (1993) estimate the annual biogenic silica production (which should be more than the net annual consumption) to be about $0.85 \text{ mol m}^{-2} \text{ yr}^{-1}$, which they believe is a conservative estimate. Our data suggest that this estimate is too low, and this may be caused by the fact that it is based on pre-spring measurements. Indeed, Pondaven et al. (2000) suggest that previous estimates of biogenic silica production are too low. Our annual silicate consumption is very similar to that reported by Sigmon et al. (2000) for the Pacific sector at 170°W .

The net silicate and carbon consumptions as calculated for the offshore Weddell Gyre are of the same magnitude. Brzezinski (1985) provided what is now seen as the classical ratio of Si:C=0.13 for uptake by (cultured) diatoms. Quéguiner et al. (1997) reported austral spring observations of the standing stocks of particulate biogenic Si and C at 6°W . At the ice edge, ratios were 0.11–0.19, suggesting some diatom abundance, and in the range of the classical ratio. Lower ratios than those for cultured diatoms also have been observed in Antarctic waters (Leynaert et al., 1991; Cota et al., 1992). In the western Weddell Sea, Si:C ratios in particulate matter were found to be as high as 0.44 (Nelson et al., 1989). Within blooms in the Marginal Ice Zone, values of 0.61 were measured in a diatom dominated population in the

Scotia Sea (Leynaert et al., 1991). Finally in diatom blooms in the Polar Front, Si:C ratios were found to be as high as 0.55–1.75 due to the presence of heavily silicified *Fragilariopsis kerguelensis* and many empty frustules (Quéguiner et al., 1997). High Si:C uptake ratios of over 0.6 also have been reported (e.g., Rubin et al., 1998). Our value of about 1 appears consistent with those for the blooms of *F. kerguelensis* in the Polar Front.

The fact that our Si:C ratio is higher than most other ratios points to a phytoplankton population in the central Weddell Gyre that on an annual basis is dominated by heavily silicifying diatoms. On a subannual basis (i.e. covering only one season or less) the phytoplankton population may be more diverse (i.e. containing more non-diatom species), which would tend to decrease the Si:C ratio. It should be mentioned that our silicate consumption may be overestimated because silicate regeneration in the surface layer is rather slow (Nelson and Gordon, 1982), and thus the seasonal silicate maximum occurs late in the season (Gibson and Trull, 1999). (Note, though, that the annual cycle of silicate as shown by Clarke and Leakey (1996) does not corroborate this). On the other hand, our silicate surface data of different months (Table 1) do not unequivocally support this mechanism, implying that the overestimation is probably minor.

5.2. Fraction export production

Priddle et al. (1998) have compiled the “annual” mixed-layer nutrient concentration deficits for several regions of the Southern Ocean, which may be compared with net annual nutrient consumptions (Table 2) for estimating the export fraction of the total primary production. This should be identical with the so-called *f*-ratio. The net nitrate export production is near the lower boundary of these nitrate deficits. Considering only Weddell Sea data, the fraction with respect to nitrogen is 40–50%. With regard to phosphate, the net consumption is definitely smaller than all deficits in Priddle et al. (1998), which range from 0.25 to 1 mmol m^{-3} (unit approximately equal to $\mu\text{mol kg}^{-1}$). Weddell Sea data result in an exported phosphate fraction of 35–55%.

Silicate is outstanding because our estimate of net consumption is near the higher boundary of deficit estimates. Some Weddell Sea deficit estimates are clearly lower than our net consumption. Thus, the fraction must be close to 1 according to these data, which seems rather high. Nelson and Gordon (1982) experimentally determined that in the (Pacific sector of the) Southern Ocean, 30–35% of the biogenic silica generated in the surface layer redissolves there, so a fraction of 0.7 would be more likely. We suppose that estimates of silicate deficits in Priddle et al. (1998) are too low. If this deficit is calculated as the difference between the winter concentration and that in summer, say January, a substantial part of the surface layer production may have been missed. Indeed, for the offshore west Weddell Sea, nutrient deficits calculated for the beginning of January (Hoppema et al., 2000) are only about one-third of the net annual nutrient consumptions as calculated in the present study. Thus, a major part of the nutrient consumption by photosynthesis has to occur in late summer and autumn, and possibly in winter (Spiridonov et al., 1996). Also algal production in the sea ice in winter may contribute (Gleitz and Thomas, 1993). Note that if the estimates of the deficit of silicate are too low, this probably also holds for the deficits of nitrate and phosphate. Thus, the fractions export production of the total production for nitrate and phosphate as given above should be considered as upper bounds.

5.3. *Uncertainties*

There are some factors that should be considered for the correct interpretation of the results. As mentioned in Section 3, the time of measurement is deemed to have an effect if we want to deduce the net nutrient consumption, i.e. the export production. The idea is that the surface layer concentrations should be the highest in winter due to both the largely completed remineralisation of organic material from the preceding growth season and upwelling of nutrient-rich deep water, all of which would lead to the smallest possible WDW–surface layer differences. Our data do not support this scenario. For nitrate, the winter surface concentrations are even the lowest, whilst for surface

phosphate there is no differentiation between the austral autumn and winter data (Table 1).

We should thus consider the possibility of active primary productivity during the wintertime, which could bias our results. Spiridonov et al. (1996) observed elevated chlorophyll and biogenic silica just north and south of our area of investigation at the prime meridian in early winter. Dieckmann (1987) even observed a wintertime bloom in this area, although in another year such an observation could not be repeated (Scharek et al., 1994). Cota et al. (1992) measured low but significant phytoplankton productivity and nutrient uptake in the western Weddell Sea/Weddell–Scotia Confluence in mid-winter. Thus, although some indications exist for active primary production (i.e. nutrient uptake) during the winter season, the reported values are generally much smaller than those for the other seasons. For our calculations, this implies that some small part of the nutrient difference between WDW and surface layer is affected by active nutrient uptake, and thus our net nutrient consumption is slightly overestimated.

A seasonal cycle of nutrients in the WDW could exist as well. In the central Weddell Gyre as part of the WDW, a layer exists that is enriched in nutrients and poor in oxygen, the Central Intermediate Water (Whitworth and Nowlin, 1987). As the export of organic matter has a strong seasonality in the Weddell Sea (Fischer et al., 1988), the WDW nutrient concentrations also may show seasonal variations. Highest WDW concentrations would then be expected in the course of the winter. However, as also in the winter the upwelling of deep water occurs and we determine the WDW–surface layer difference due to upwelling, the possible high concentrations in the WDW would fully comply with our assumptions. Moreover, the consistency of our surface layer–WDW differences during different months (Table 1) suggests that the effect must be small.

Another factor that may influence our results is dissolved organic matter (DOM) and particulate organic matter (POM), if these would accumulate seasonally in either the surface layer or the WDW. This would effectively decrease the nutrient concentrations in these layers. Total organic carbon (TOC, which includes both DOM and

POM) data from the Weddell Sea reveal that the variation in the WDW is small and that winter-like surface values are almost equal to those in the WDW layer (Wedborg et al., 1998). As this holds for organic carbon, we infer that it also holds for organic nitrogen and phosphorus. Moreover, the organic matter concentrations are, apart from within blooms, relatively low (Wedborg et al., 1998). Indeed, Cota et al. (1992) report particulate organic nitrogen and biogenic silica concentrations for the wintertime Weddell–Scotia region that are much lower than those in the vegetative period. Therefore, DOM and POM effects are probably negligible in our calculations.

6. Conclusions

Our method of chemically balancing the surface water and WDW layers has proven to be powerful because it allows a direct estimation of the export production, a parameter that has been difficult to obtain integrated over large scales of time and space. It renders consistent results for nitrate and phosphate, and also interannual variation is small. Our method requires only moderate logistic effort to obtain an annual estimate. An inconvenience, however, may be that autumn/winter data are required, which could be hard to collect due to prohibitive weather conditions in the Southern Ocean. In addition, the residence time of the surface layer is required, which must be obtained from additional data or model results.

Our estimate of export production includes both particulate and dissolved organic material, whereas sediment traps only collect the former. Our estimated export production is considerably higher than that based on sediment-trap data (Wefer and Fischer, 1991). This is consistent with the notion that a large part of the export is already consumed in the upper parts of the water column (Suess, 1980; de Baar et al., 1983). Indeed, Nelson et al. (1996), based on data from the Ross Sea, warn that the export production as measured below the surface layer hinges on the depth at which the export has been determined. Measuring export at 200 m in the Ross Sea, though, leads to a consistent picture of the nitrogen budget (Smith

and Asper, 2000). Occasionally, bacteria may consume up to 100% of the primary production (Gleitz et al., 1994), causing a great reduction of sinking detritus and a large flux of dissolved material. This indicates that at least occasionally dissolved organic matter may play some role.

Although the central Weddell Gyre is commonly considered to be less productive, we found export productions of fairly large magnitude, particularly for silicate. The silicate to carbon export ratio of about 1 is very high. High Si:C ratios in particles have been found before in Antarctic waters, but it is thought that these findings are exceptional and spatially restricted (Nelson et al., 1995). Our study suggests that this is not the case. Contrary to other studies, which extrapolate some seasonal data to an annual estimate (introducing large uncertainties), we give annual data that are indeed based on real annual changes. This considerably enhances the reliability of our estimation.

We found significant variations of nutrient concentrations in the WDW layer (Table 1). It is possible that these are caused by the seasonally varying degradation of organic matter sinking from the surface layer. A close interaction between this process and upwelling of deep water is anticipated, which has impact on the nutrient composition of the upwelled water. Such interactions also may exist for other biologically mediated properties (carbon dioxide, iron). More detailed investigations of these important interactions are therefore required.

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